

*The Refractive Indices of Sulphuric Acid at Different Concentrations.*

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During the past 60 years various determinations have been published of the refractive indices of sulphuric acid for different concentrations and different rays for the purposes of tracing out the relationships between the refractive energies, dispersion, and chemical constitution. Some observers have published isolated determinations, others more or less connected series, according to the object in view.

Baden Powell\* appears to have been the first to give values of the refractive indices of the Fraunhofer lines B, C, D, E, F, G, and H for a sample of acid  $d\ 18\cdot5/? = 1\cdot835$  (about 94·5 per cent. concentration), though the temperature of the water density is not given. The object of this work was for the purpose of comparing the observed results for  $\mu_B$ , etc., with those calculated by Sir W. R. Hamilton's modification of Cauchy's dispersion formula.

Van der Willigen's† investigation remains after the lapse of 36 years the most complete study of the subject; his observations were for 13 Fraunhofer lines, and 17 samples of acid of concentration varying from 0·34 per cent. to 95·61 per cent.; from the results curves are drawn to express the relation of  $\mu$  and the constants of Cauchy's formula with percentage concentration.

These last were determined by the densities, ascertained by a hydrostatic method and compared with a table of Bineau's construction; subsequently the percentage values have been re-calculated by Pickering‡ and the Kaiserliche Normal-Eichungs Kommission.§

\* 'Undulatory Theory as applied to Dispersion of Light,' London, 1841; also 'British Association Report,' 1839, and 'Transactions Ashmolean Society,' vol. 1, 1836.

† 'Archives Musée Teyler,' vol. 1, p. 74, Haarlem, 1868.

‡ 'Journ. Chem. Soc. Trans.,' 1893, vol. 99.

§ 'Wissenschaftliche Abhandlungen der Kaiserlichen Normal-Eichungs Kommission, Part V, Berlin, 1904. Shortly after the present work was commenced, the Directorate of the Commission courteously presented to one of us (V. H. V.) a copy of this report upon the densities and coefficients of expansion of sulphuric acid-water mixtures, together with a recalculation of the values obtained by previous observers. This report has proved of great service to our work; it will be alluded to in the sequel by the abbreviation K.N.E.K., as sanctioned by the usage of the writers of the memoir.'

The principal conclusions arrived at by Van der Willigen may be summarised briefly as follows:—

1. Biot and Arago's general formula

$$(100-p)(\mu^2-1)/d + p(\mu'^2-1)/d' = 100(\mu''^2-1)/d'',$$

in which  $p$  = percentage,  $\mu$ ,  $\mu'$ ,  $\mu''$ ,  $d$ ,  $d'$ , and  $d''$  are the refractive indices and densities for sulphuric acid, water and the mixtures respectively, is not applicable.

2. The maximum refractive index occurs between the concentrations 81·41 per cent. and 85·98 per cent., corresponding approximately to the mono-hydrate  $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  (84·5 per cent.); there are also well-marked alterations in the coefficients  $B$  of Cauchy's dispersion formula of the form

$$\mu = A + B/\lambda^2 + C/\lambda^4$$

at about 72 per cent., or the point of maximum contraction of mixtures of sulphuric acid and water.

3. For more dilute solutions an empirical equation  $\mu = A + bp + cp^2$  appears to hold good.

Handl and Weiss\* gave values of  $\mu$  for the Fraunhofer lines A, B, C, D, E, and F for sulphuric acid  $d 20/° = 1\cdot8513$  mixed with successive quantities of water to obtain 9/10, 8/10, etc., concentration. From the densities the percentage values have been recalculated by Gladstone and Hibbert.† The object of their investigation was to trace out the relation between the contraction on admixture and the retardation-coefficient, namely,  $C/\theta, C = \text{contraction}$ , and

$$\theta = \frac{\mu''(V + V_2 + CV_1V_2) - V_1\mu + V_2\mu''}{V_1V_2\mu'\mu''},$$

in which  $\mu, \mu', \mu''$  have the same significance as above,  $V_1$  and  $V_2$  the volumes of the acid and water respectively, and  $V$  that of the mixture.

Gladstone‡ gave the values of  $\mu_A$ ,  $\mu_D$ , and  $\mu^H$  for nine samples of sulphuric acid of specific gravity varying from 1·118 to 1·843 (the latter determinations being apparently made at different temperatures), in order to determine the refraction-equivalents of the acid itself.

In a subsequent communication the same author, with Hibbert§ gives the values for  $R_a$ ,  $R_D$ ,  $R_B$ , namely, the refractive energies for these three lines for 20 samples of sulphuric acid of percentage concentration varying from 3·25 to 97·5 per cent. Unfortunately only the refractive index for water is given,

\* 'Wien. Akad. Ber.', vol. 30, p. 389, 1858.

† 'Jour. Chem. Soc. Trans.', 1895, p. 866.

‡ 'Phil. Trans.', vol. 160, p. 9, 1870.

§ 'Journ. Chem. Soc. Trans.', 1895, p. 866.

and not those of the mixtures, nor determinations of the densities, though determined with an error of 1 in 8000, which is fairly large.

It appears that from the original determinations the refractive energies were calculated, that of the water deducted and the remainder taken as that of the acid, a method which, as the authors themselves admit, throws all the errors, whether experimental or arising from impurity, upon the acid. The purport of the argument is to show that the molecular refraction varies but little with the concentration, though subsequently it is shown by a curve that "there is a sudden increase when a little water is added to the anhydrous acid, and after that a slow decrease." The curve given, however, appears to be an abridgment of the curves of Van der Willigen expressed in different terms, and with the errors consequent upon the methods adopted.

It further appears that the method of calculation and reasoning therefrom is at variance with the conclusion of Van der Willigen that a formula such as that proposed by Biot and Arago is unsuitable.

Le Blanc\* made seven determinations of the density and  $\mu_D$  of acids varying in concentration from 4·78 to 94·11, and showed that the values of  $M(\mu_D - 1)/d$  for sulphuric acid increases nearly uniformly with the dilution, and from a comparison of these values with those of sodium sulphate, which have a constant value, he infers that the variation in the former case is due to the hydrogen ion with probable exclusion of the sulphonion ion.

Hallwachs† gave the ratios of V (dilution as gramme/litre),  $V\Delta n \cdot 10^2$  (molecular refraction change), and coefficient of ionisation, and his values show that the two latter increase as the molecular dilution increases.

Pickering‡ recalculated Van der Willigen's results, and gave a rough illustration of the curve of refractive index in terms of percentage concentration, from which it is concluded that the maximum value of the refractive index corresponds with the composition of the monohydrate  $H_2SO_4 \cdot H_2O$  (84·5 per cent.  $H_2SO_4$ ) and there are minor alterations at about 60 per cent., nearly corresponding to the composition of the tetrahydrate  $H_2SO_4 \cdot 4H_2O$ , and another about 24 per cent. After alluding to possible sources of error in Van der Willigen's determinations, Pickering expresses the opinion that "a full series of observations would supply further important evidence as to the nature of sulphuric acid solutions."

From this résumé of literature it appears that the different observers have viewed their results from entirely different standpoints. The recent investigations of Knietzsch§ on the remarkable alteration in the physical and

\* 'Zeits. Physikal. Chem.', (4), p. 533, 1889.

† 'Wied. Ann.', vol. 47, p. 391, 1892.

‡ 'Jour. Chem. Soc. Trans.', 1893, p. 99.

§ 'Ber.', vol. 34, p. 4069, 1901.

chemical properties of sulphuric acid containing 97 to 98 per cent. sulphuric acid, and our own determinations\* of the refractive indices of nitric acid induced us to take up the subject with especial reference to the more concentrated solutions, and to the variations, not only of refractive indices, but also of dispersion constants (a subject largely neglected), with percentage strength or molecular dilution.

*Determination of Concentration.*

The concentration was ascertained by means of the densities, which also serve as factors in the Gladstone-Dale, Lorentz formulæ, and the results at  $15^{\circ}/4^{\circ}$  ascertained by Table I of the K.N.E.K. report. Various forms of the U-tube pyknometer were at first tried, but in the case of the more concentrated acids, the risk of absorption of water during the necessary operations appeared to be too considerable. Eventually the capillary bottle pyknometer (of 25 c.c. capacity) was adopted, covered with a glass plate, as used by Mendeleef and Pickering, and weighed against a sealed-up similar bottle as a tare, a very necessary precaution, as pointed out in the K.N.E.K. report p. 216, and more particularly worked out by one of us (J. J. M.).† Each determination was made in duplicate, one with a rising the other with a falling thermometer, the pyknometer being kept in each case in the water bath for about an hour, when it was supposed that the innermost core of acid had attained to the same temperature as the outer portions; the errors of temperature, as recorded by the thermometer, probably did not exceed  $\pm 0.01$ . The maximum difference in the two duplicate experiments was about 3 milligrammes for the more concentrated acids, and less for those of lower strength; if the mean value, 1.5 milligrammes, is adopted, an error is implied of 0.0001 in density.

For the thermometer (Gerhardt 5543 Jena glass) ( $1^{\circ} = 15$  mm.) used, the following calibrations were undertaken:—(1) Of scale reading by a Hilger travelling microscope, itself calibrated against a metre standard divided into millimetres; (2) of thread-length by Gay-Lussac's method as modified by Thorpe and Rücker‡; (3) of zero displacement; the readings were reduced to the international hydrogen scale by Scheel's tables for Jena glass 16'''§. The temperature, as recorded, is thus in accord with that adopted by the K.N.E.K.

The reduction factor for water at  $15^{\circ}$  was taken from Thiessen, Scheel and

\* 'Roy. Soc. Proc.,' vol. 69, p. 86, 1901, and 'Phil. Mag.' (6), vol. 3, p. 118, 1902.

† 'Proc. Roy. Soc. Edin.,' 1902, p. 358.

‡ 'British Association Report,' 1882, p. 145.

§ 'Wied. Ann.,' vol. 58, p. 168, 1896.

Diesselhorst's\* values, and those for reduction of the weighings to vacuum from Kohlrausch's tables.†

As it is not desired to contribute further to the accumulated literature on the densities of sulphuric acid, one example only need be cited to illustrate the degree of concordance of our results with those of previous observers.

The density was determined of a sample of acid supplied by Dr. Messel, purified by frequent crystallisation of the concentrated acid, and similar to those used by W. H. Perkin, sen.,‡ and Pickering§ in their investigations. The value obtained at 15/4 was 1·83736, that calculated by the K.N.E.K. (Report, p. 163) from Perkin's observations at 15/15, 20/20, and 25/25, and reduced to the hydrogen scale is 1·83743, or a difference of 0·00007 in density and of 0·01 in percentage value, namely, 99·62 as against 99·61 per cent.

#### *Determination of Refractive Indices.*

The spectrometer, quartz prism with its fittings, and the general methods of observation were precisely as described in our previous work|| on nitric acid solutions, so that it is only necessary to give a brief description and add a few remarks upon the further results of our experience.

The spectrometer, for the continued loan of which we are indebted to the Government Grant Committee of the Royal Society, was obtained from Becker (Meyerstein's successor). Its graduated circle is 27 cm. diameter, and reads directly to 1/10°; it is furnished with two reading microscopes, supplied with micrometers, three revolutions of which correspond to one scale-division; as the micrometer screw heads are divided into 60 parts, an observer is enabled to read directly to two seconds. The circle was calibrated by both the telescope and plumb-line methods, which we have described.¶ The dimensions of the plates of the quartz prisms were 75 mm. × 68 mm. × 6 mm., of the aperture 20 mm., and the angle of the prism about 60° 6'. The plates were cemented on by paraffin, purified by sulphuric acid, and then frequently by water; it did not appear that any subsequent action between the acid and the paraffin occurred in the course of the observations.

It was found that vibrations due to traction engines, wagons, etc., passing

\* 'Wied. Ann.', vol. 60, p. 340, 1897.

† 'Leitfaden,' p. 408.

‡ 'Journ. Chem. Soc. Trans.', 1886, p. 782.

§ 'Journ. Chem. Soc. Trans.', 1890, p. 73.

|| Cf. reference (p. 472).

¶ Drude's 'Annalen der Physik,' vol. 4, p. 575, 1901.

along the street, situated some 35 yards from the laboratory, might produce a variation in reading of as much as  $20''$  of arc; these vibrations doubtless caused some displacement of adjusting screws or springs. The errors arising from these variations were duly corrected.

The angle of the prism was found to vary about  $10''$  in different rebuildings, sometimes in one and sometimes in the other direction; its value was, therefore, taken every few days. The two extreme values were  $60^\circ 6' 0''$  and  $60^\circ 6' 24''$ .

As in our previous work the minimum deviation was determined at three different temperatures; from the values obtained the coefficient of variation per degree temperature was calculated out, and from its mean value the minimum deviation at  $15^\circ$  was estimated, and this used for the recorded value of  $\mu$ . One series of observations will serve to illustrate this adopted method.

Concentration of sample,  $85.92^\circ$ . Line D.—

(a)	Minimum deviation .....	$32^\circ 6' 42''$	at $13.6$
(b)	" "	$32 4 2$	$15.5$
(c)	" "	$32 11 22$	$10.1$

Variation of minimum deviation per degree temperature (K)—

From (a) and (b) .....	K = $84''$
(a) (c) .....	K = $80$
(b) (c) .....	<u>K = <math>82</math></u>
Mean.....	$82''$

Using the above variation, the corrected values for minimum deviation at  $15$  appear as under—

$$\left. \begin{array}{l} (a) 32^\circ 4' 51'' \\ (b) 32 4 47 \\ (c) 32 4 44 \end{array} \right\} \text{Mean value ..... } 32^\circ 4' 47''$$

Value of  $\mu^{15}_D$  calculated from above =  $1.438632$ .

In some of the later experiments the above method was slightly modified as follows: observations were made at every  $1/5^\circ$  through one whole degree with the thermometer rising very slowly; from these the mean value of the minimum deviation at the mean temperature was calculated. The temperature was then raised slowly about  $2^\circ$ , and a second series of observations made at every  $1/5^\circ$ , which were dealt with similarly. Finally, the two sets of observations were compounded together, and their mean taken at mean temperature; the value thus obtained was the result of 10 distinct determinations.

*Spectrum Lines Used.*

The sodium line and the three hydrogen lines  $H_{\alpha}$ ,  $H_{\beta}$ , and  $H_{\gamma}$ , were used for the determinations; the first was obtained by a flame, and the three last from two Pflücker tubes of slightly varied construction. It was found after several attempts that the line  $H_{\delta}$  was not practicable to deal with, a result in accordance with observations of other workers upon refractive indices. The wave-lengths of the four lines used were taken as 589·3 (mean of  $D_1$  and  $D_2$ ), 656·3, 486·1, and 434 millionths millimetre respectively.

*Magnitude of Error.*

Adopting all the corrections detailed in the present and previous communication, we believe that the errors in the values of  $\mu$  do not exceed a few units in the sixth places of decimals for acids below 90 per cent. concentration; above this the error may amount to one unit in the fifth place. At present one of us (J. J. M.) is engaged upon devising a method of overcoming the experimental difficulties in dealing with acids of the highest concentration.

*Samples of Sulphuric Acid.*

We are indebted to Dr. Messel for a liberal supply of two samples of acid (both of which had been purified by frequent crystallisation), one labelled *concentrated* acid and stated to be of 99·7 per cent. strength, the other labelled *catalytic* acid, and stated to be of 99·5 per strength. The values found by us by the densities at 15/4 according to the K.N.E.K. tables were 99·62 and 99·4 respectively; these slight differences are within the errors of observation. The values found for  $\mu$  and  $d$  for these two acids were compared at nearly the same concentration, 76·31 and 76·59 respectively; they differed only so far as the differences of concentration. These acids may, therefore, be taken as identical in physical properties, though their past history of manufacture was different.

A third sample, used for one determination only in the present work, was purchased of Herr E. Merck, of Darmstadt, as of 1·84 density; the value found at 15/4 was 1·84161, which is slightly higher than the maximum 1·84148, found by the K.N.E.K. at 97·3 per cent. The difference, 0·00013, corresponds to error in weighing of the acid of 2 milligrammes, or a difference of temperature of about 0·11.

Certain tests were made to ascertain the purity of the several samples of acid as follows:—

1. *Organic matter* and *sulphurous acid* 0·1 c.c. permanganate solution (containing 0·1 milligramme available oxygen) added to 10 c.c. acid and 20 c.c. water. Catalytic acid, trace of these impurities, concentrated and Merck's acid. free.

*Chlorine* by dilute silver nitrate solution added to acids diluted as above. Concentrated acid, minute trace, catalytic and Merck's acid free.

*Nitric Acid*.—By addition of diluted acids to a crystal of brucine, all acids free.

*Nitrous Acid*.—By the meta-phenylene diamine test, which according to our previous investigations will reveal the presence of 1 part in  $15 \times 10^7$  of this impurity. Concentrated and catalytic acids at limit of delicacy, Merck's acid beyond the limit.

*Ammonia*.—An excess of soda solution free from ammonia was added to 10 c.c. of each sample of acid, and then 2 c.c. of Nessler's solution added. A faint yellow tint was produced in the case of all three acids, indicating a slight trace of ammonia, which would produce no effect on the results.

#### *Purification of Water used for Dilution.*

Ordinary tap water was boiled for some time in an open copper boiler to drive off dissolved gases and other volatile matter; the boiler was then closed and the steam passed into two boiling dilute solutions of potassium permanganate (the first slightly acidified, with sulphuric acid, the second, strongly alkaline), which were contained in bolt-head Jena glass flasks of about 1 litre capacity. The steam then passed through a form of spray tap, which proved highly efficient, and thence into a condenser with a block-tin inner tube; the water dripped into a bottle, invariably steamed out previous to use. Though rubber stoppers were used in the apparatus, yet it was found that if these had been well steamed previously, no sensible amount of impurity was imparted to the water.

The specific conductivity  $\text{Kem}^{-1} \text{ ohm}^{-1}$  of numerous samples of this water was determined as a test of purity; it varied from  $1.2 \times 10^{-6}$  to  $1.5 \times 10^{-6}$ . The former value does not differ widely from that ( $0.96 \times 10^{-6}$ ) found by Kohlrausch and Maltby\* for water specially purified, but not distilled in vacuum, which last has a value of  $0.04 \times 10^{-6}$ . The above investigators from the observations of Knox† have traced the difference to dissolved carbon dioxide. Adopting the data of the latter, the molecular proportion of carbon dioxide in our samples of water would vary from 0.000057 to 0.000081 gramme equivalent litre, or a quantity which can with all reason be assumed to be insufficient to produce any sensible difference in the determinations of refractive index.

The value found for water prepared according to the method described above was  $\mu_B^{15} = 1.333468$ ; as this is lower than the value found by others,

\* 'Wiss. Abh. Reichsanstalt,' vol. 3, p. 193, 1900.

† 'Wied. Ann.,' vol. 54, p. 54, 1895.

as also by ourselves in our former work, it was thought desirable to repeat the observations, and the results are briefly tabulated as under:—

Water. Mean conductivity,  $K = 1.3 \times 10^{-6}$ .

Temperature.	No. of observations.	$\delta_{15}$ (reduced).
19.2	4	23° 40' 57''
14.8	4	23 40 59
14	3	23 40 59
14.5	1	23 40 57
15.1	4	23 40 56

The mean value of the 16 observations is  $\delta_{15} = 23^{\circ} 40' 58'' \pm 0.23''$ ; the refracting angle of the prism, rebuilt for the purpose, was  $60^{\circ} 6' 20''$ ; hence  $\mu_D^{15} = 1.333393$ , still slightly lower.

In order to determine whether the discrepancy was due to dissolved carbon dioxide, in however small a proportion, or to dissolved silica, the following series of experiments were conducted.

Firstly, as to carbon dioxide, the gas was prepared from marble and dilute hydrochloric acid, both of reasonable purity; it was washed with water and then passed through a tube about  $\frac{1}{2}$  metre long, packed with marble, the further end of which was drawn out and bent round, so that the gas might be delivered into the water contained in the prism and impurity due to rubber connections avoided.

To ascertain the efficacy of the apparatus for the purpose required, the packed tube was first steamed out and then the gas passed into water to the point of saturation. The solution thus obtained was free from all trace of hydrochloric acid.

The results of the observations upon the effect produced by the solution of the carbon dioxide are given below:—

No. of experiment.	$\mu_D^{15}$ .	Remarks.
I .....	1.333386	Volume of gas dissolved about 1.5 c.c.
II .....	1.333371	" " 3.0 c.c.
III .....	1.333335	Water saturated.
IIIA.....	1.333365	Solution III after standing for 13 hours.

It is evident from these results that the presence of carbon dioxide decreases the refractive index of water, and the greater the amount so dissolved the lower the value, and conversely, if the gas passes out of solution the value is increased.

Secondly, as to silica; a crystal of quartz was boiled in nitro-hydrochloric

acid, then with highly purified water; it was then ignited and quickly dropped into water; the powder thus obtained was frequently washed.

The results of the observations are given below:—

Value of  $\mu_D^{15}$  for a freshly prepared sample of water = 1.333393.  
" " left in contact with quartz for 13 hours = 1.333371.

The presence of silica also reduces the value of the refractive index, though only to a degree almost inappreciable. So far as we are aware there has been no investigation upon the solubility of silica in water as determined by the method of electric conductivity.

The case of the discrepancy between the value of the refractive index as found by ourselves and previous observers may be summarised as follows:—

Our lower value might, so far as the observations upon the effect produced by carbon dioxide indicate, be due to that cause, but, on the other hand, the frequently repeated determinations of the electric conductivity show that the amount of this impurity present was insignificant, being not greater than that found by other workers for samples of water carefully rectified, but not distilled in vacuo. The lower value might also be due to silica, though the alteration produced by this substance is very slight even in extreme circumstances.

On the other hand the higher value found by previous observers might be due to the solution of alkalies and other metallic oxides from the glass used for the prisms.

It would require a prolonged series of experiments to decide this matter, and as the refractive index of pure water is only incidental, so far as regards the present investigation, we prefer only to state the case and to leave it as a subject of further enquiry.

#### *Results.*

In the following table are given in Column I the reference number of sample, in Column II the percentage value as deduced from the density, and in Columns III–VI the values of  $\mu$  reduced to 15° C. for the four lines H<sub>a</sub>, D, H<sub>b</sub> and H<sub>y</sub>, respectively.

Table I.

I.	II.	III.	IV.	V.	VI.
1	0·84	1·332805	1·334664	1·338807	1·342029
2	1·76	333944	335794	339984	343181
3	3·88	336416	338313	34249	345704
4	5·1	337896	339855	343964	347326
5	9·58	343485	345361	349633	352955
6	14·0	349001	350953	355233	358576
7	18·31	354322	356297	360653	363939
8	22·16	359194	361248	365598	368854
9	25·9	364051	36605	370506	373882
10	29·24	36811	370196	374726	378211
11	30·86	370161	372280	37683	380248
12	34·35	374213	376332	380948	384426
13	38·48	379184	381388	386002	389530
14	42·45	384119	38635	39099	394507
15	46·46	388987	391184	395934	399508
16	52·24	396336	398589	403405	406851
17	56·22	401655	403907	408767	412274
18	59·65	406267	408582	413445	416976
19	62·88	410536	41285	417767	421437
20	66·44	415487	417822	422782	426452
21	69·6	419838	422156	427177	430848
22	72·28	423549	42595	430943	434584
23	74·86	426858	429185	434234	437933
24	76·3	428767	431132	436185	439887
24(bis)	76·59	42903	431388	436494	440167
25	78·09	430841	432023	438242	441983
26	80·05	432946	43529	440335	444079
27	80·43	43323	435628	440658	44438
28	81·77	434442	436818	441871	445582
29	83·2	435459	43782	442875	44657
30	84·56	436051	438403	443417	447071
31	85·50	436267	438632	443603	447277
32	85·92	436272	438632	443651	447384
33	86·37	436246	438591	44357	447324
34	87·40	436065	43841	44341	447031
35	90·53	43418	436468	441361	449978
36	95·33	430862	433061	437836	441402
37	97·3	425367	427482	432064	435420
38	98·7	41947	421558	426025	429396
39	99·3	418387	420450	429845	428206

We give by way of comparison the results obtained by Van der Willigen\* and ourselves for four acids of approximately the same concentration. The former have been reduced as to densities to the hydrogen scale, and as to percentages to modern atomic weights by the K.N.E.K., and to a temperature of 15° by the temperature coefficients found by ourselves.

The agreement, having regard to the large number of corrections involved and to the difference of purity of water and acid, is for the most part satisfactory except for H<sub>2</sub>. The diversity in the last case may arise either from differences of method, Van der Willigen using a heliostat of the Fahrenheit type and a 1/100-inch grating, as against our Pflücker tube, or to

\* *Loc. cit. supra.*

Table II.

	V. d. W. 38·63 per cent.	V. and M. 38·47 per cent. (38·63 corr.).	Diff.	V. d. W. 56·23 per cent.	V. and M. 56·22 per cent.	Diff.
H <sub>a</sub>	1·37984	1·37937	+ 47	1·40185	1·40166	+ 19
D	38113	38158	+ 45	40419	40391	+ 28
H <sub>s</sub>	38678	38619	+ 59	40888	40877	+ 11
H <sub>r</sub>	39054	38972	+ 82	41257	41227	+ 30
	72·14 per cent.	72·28 per cent.		81·68 per cent.	81·77 per cent.	
H <sub>a</sub>	1·42315	1·42336	- 21	1·43453	1·43444	+ 9
D	42565	42575	- 10	43695	43682	+ 13
H <sub>s</sub>	43067	43074	- 7	44195	44188	+ 7
H <sub>r</sub>	43472	43438	+ 34	44605	44558	+ 47

the angle  $34^\circ 15'$  of the prism used by the former, which, as he himself admits, was smaller than desirable, or to both causes combined.

#### *Temperature Coefficients.*

The values, up to the concentration 22·16, expressed in terms of  $10^{-6}$  and calculated as explained above, are given below:—

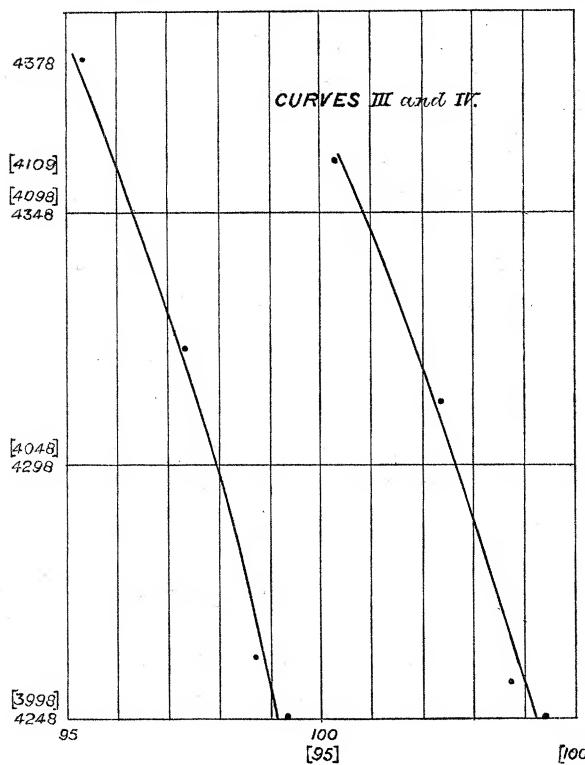
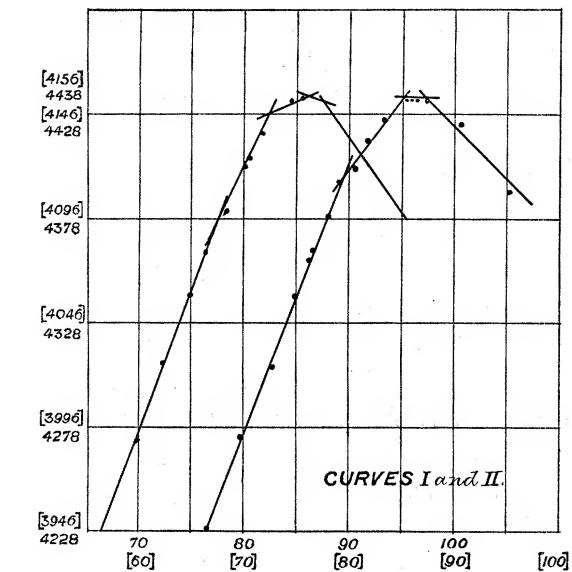
Table III.

Concentration.	Temperature coefficient.	Concentration.	Temperature coefficient.
0·84	86	9·58	150
1·76	101	14·0	170
3·83	101	18·31	213
5·1	130	22·16	256

The coefficients beyond this point are practically constant within the limits of experimental error, with a slight maximum between the concentrations 84–87 per cent., from which there is a tendency towards a minimum.

It will be evident from the data given in Tables I and III that the refractive indices increase uniformly up to a concentration of about 76 per cent., thence more gradually to the maximum point at or about 85·5 per cent.

The values of  $\mu$  for H<sub>B</sub> and A<sub>D</sub> (the latter being shifted 10 units along the abscissæ axis to the right to avoid too much overlapping), in terms of percentages from 66 to 94 per cent., are illustrated in Curves I and II, from which it is manifest that these values may be represented as linear functions of the percentages, though it is possible that about the maximum point the



results might be represented upon a curve to which the straight lines depicted are tangential. Curves III and IV (on a more open scale) illustrate

the results from 94 to 100 per cent. in like manner; these show a distinct curvature, probably of a hyperbolic type.

The most definite, namely, the maximum point, corresponds approximately with the composition of the hydrate  $\text{H}_2\text{SO}_4\text{H}_2\text{O}$  (84·48 per cent.), though slightly above it, as previously observed by Van der Willigen.\* Less marked points occur at about 76 for  $\mu$  and at 66 per cent. for Cauchy's constant B, which again correspond only approximately with the hydrates  $\text{H}_2\text{SO}_4\text{H}_2\text{O}$  (73·13 per cent.) and  $\text{H}_2\text{SO}_4\text{H}_2\text{O}$  (64·47 per cent.). As we have pointed out in a previous communication,† the points of discontinuity are to some extent ideal, in that an apparently abrupt change of events can be resolved into a gradual transition stage. It is not our purpose to deal further with the question of the existence or non-existence of hydrates in solution, as it has been so fully and fairly discussed, and the literature thereon so carefully collated by Drs. Domke and Bein‡ quite recently, that any further remarks on our part would be superfluous.

The irregularities observed from 95 to 100 per cent. will be considered in a subsequent section.

#### *Refraction Equivalents.*

As mentioned above, the molecular refraction equivalents of the sulphuric acid as the differences between those of the several solutions and the water contained therein have been calculated by Gladstone and Hibbert§ according to the factor of the former  $(\mu - 1)/d = \text{constant}$ .

But, on the one hand, such a method of treatment does not appear to us to be reasonable, and on the other the factor is only empirical. Though we have calculated out the values of  $(\mu_D - 1)/d \cdot 10^{-5}$  for the various solutions, and found that they decrease approximately as a linear function of the concentration, yet we refrain from giving these data, as less satisfactory than those obtained by using the more rational factor of Lorentz.

In Table IV are given respectively in Column 1 the concentrations, in Column 2 the calculated values for  $(\mu_{\text{H}_2}^2 - 1) (\mu_{\text{H}_2}^2 + 2) d$  (hereafter designated  $R_{\text{H}_2}$ , etc., for the sake of brevity).

The values of the factor  $\Delta R/\Delta p$  up to a concentration of 90 per cent. vary only by one or two units from 70, having regard to errors of experiment.

This relation,  $\Delta R/\Delta p = \text{constant}$  may be put into the form of an equation

$$R_1 = R - a\Delta p,$$

\* *Loc. cit. supra.*

† 'Roy. Soc. Proc.', vol. 69, p. 119, 1901.

‡ *Of. reference above; 'Zeits. Anorgan. Chem.', vol. 43, pp. 153 to 155 and 178 to 181, 1905.*

§ *Loc. cit. supra.*

Table IV.

Concentration.	$R_{H\alpha}$ .	Concentration.	$R_{H\alpha}$ .	Concentration.	$R_{H\alpha}$ .
0·84	20452	38·48	17887	78·09	15129
1·76	20390	42·45	17605	80·43	14970
3·88	20245	46·46	17325	81·77	14877
5·1	20160	52·24	16918	83·2	14781
9·58	19862	56·22	16642	84·56	14694
14·0	19561	59·65	16400	85·92	14598
18·31	19265	62·88	16169	87·4	14500
22·16	19003	66·44	15936	90·53	14294
25·9	18752	69·6	15708	95·33	14037
29·24	18516	72·28	15527	97·3	13895
30·86	18408	74·86	15347	98·7	13738
34·35	18160	76·3	15241	99·3	13715

in which  $R$  is the value for any concentration taken as an origin of co-ordinates, and  $a$  the constant. But a closer inspection of figures and the calculation of data from the above equation show that there is a slight alteration at about 30 per cent., not amounting to more than 1·5 per cent. in the factor. It is not desired to lay too much stress upon this change, which is of the nature of a very gradual transition, but merely to mention that this is the point of maximum electric conductivity as observed by Kohlrausch\* and others, and also a point of variation in the factors of other physical properties.

Otherwise the evidence is against the existence of hydrates or, to put the case in another form, it matters not whether the water is combined either with the sulphuric anhydride or the sulphuric acid, or combined with neither.

The exceptional values of  $\Delta R / \Delta p$  for the four several lines for the higher concentrations are given below:—

Table V.

Concentration.	$H_\alpha$ .	D.	$H_s$ .	$H_\gamma$ .
90·53	66	69	69	67
95·33	53	46	50	51
97·3	71	90	90	87
98·7	112	115	115	113
99·3	38	33	35	36

In the succeeding table the differences, in terms of  $10^{-5}$ , are given between the values of the Lorentz equivalent observed, and those calculated from the general formula  $R_1 = R - a \Delta p$ , the two lines selected being D and  $H_\gamma$ , namely, the most and least practicable for observation purposes.

\* 'Pogg. Ann.', vol. 138, pp. 238, 370, 1869; *ibid.*, vol. 151, p. 378, 1874, etc.

For the D line  $\alpha = 68.5$ ,  $R = 20,348$  between the limit 3.9 and 29.2 per cent., and  $\alpha = 68.9$ ,  $R = 18,501$ , between the limits 30.8 and 90.5 per cent.; similarly, for the  $H_{\gamma}$  line,  $\alpha = 70.5$ ,  $R = 20,963$ , between 0.9 and 29.2 per cent., and  $\alpha = 72$ ,  $R = 18,869$ , between 30.8 and 90.5 per cent.

The greatest difference between the observed and calculated results amounts in one case only to 40 in 14,000, but in the large majority of cases to less than one-fourth of this, which is within the limits of experimental error.

In Curve V the percentages are given along the abscissæ axis, and the values of the Lorentz factors (to four places) as ordinates; the former are for the purpose of abbreviation divided into three sections, namely, from 0 to 30, 30 to 60, and 60 to 92 per cent. respectively.

Table VI.

Percentage.	Difference.		Percentage.	Difference.	
	D.	$H_{\beta}$ .		D.	$H_{\beta}$ .
0.84	—	—	62.88	-19	-19
1.76	—	-3	66.44	-20	-14
3.88	—	-9	69.6	-15	-11
5.1	+3	0	72.28	-7	+5
9.58	-6	+1	74.86	-11	+1
14.0	-7	+1	76.3	-28	-14
18.31	+1	-5	78.09	+9	+13
22.16	+6	0	80.05	+21	+6
25.9	+3	+5	80.43	-3	+4
29.24	0	+4	81.77	0	+11
30.86	—	—	83.2	+3	+13
34.35	-6	-13	84.56	+53	+8
38.48	+6	0	85.5	+12	-16
42.45	+5	-6	85.92	+8	+18
46.46	-10	+24	86.37	+8	+18
52.24	-7	-10	87.40	+11	+12
56.22	-12	-12	90.53	+22	+40
59.65	-12	-24			

These results are in general accordance with those which we obtained in the case of nitric acid, the only points of difference being the value of the constant, namely  $70 \cdot 10^{-5}$  instead of  $(40 \text{ to } 50) 10^{-5}$ , and the fewer transition stages. It is possible that the difference of the factor is mainly due to the presence of a second hydroxyl grouping, more especially as recent investigations\* upon dielectric constants ( $K$ ) have shown that the presence of such hydroxyl groupings increase the value beyond that required for the right hand side of the original equations of Lorentz,

$$(\mu^2 - 1)/(\mu^2 + 2) d \quad \text{and} \quad (K - 1)/(K + 2) d \quad \text{each constant.}$$

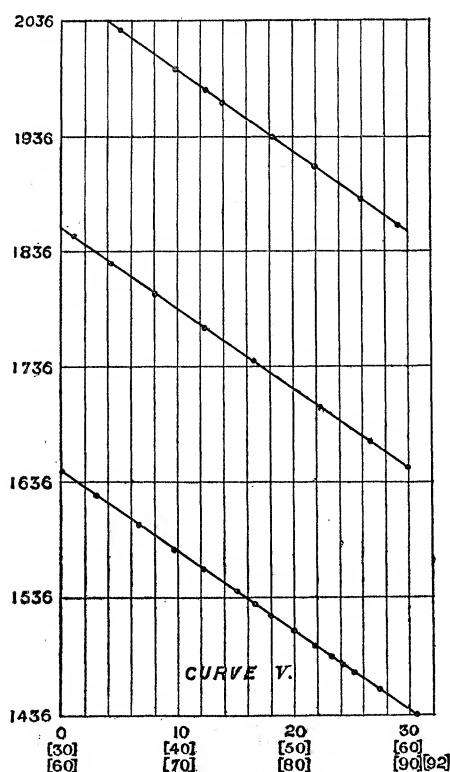
\* Thwing, 'Zeits. Physikal. Chem.', vol. 14, p. 286, 1894.

Unfortunately neither the observations at present accumulated\* nor the degree of accuracy desirable are sufficient to determine whether an equation of the form

$$(K' - 1)/(K'_2 + 2) d = (K - 1)/(K + 2) d - a\Delta p$$

would hold good.

However this may be, if we consider the concentrations from 3 to 95 per cent., though the density according to the various memoirs on the subject



is a very complicated function of such concentrations, yet the factor  $(\mu^2 - 1)/(\mu^2 + 2)$  is a linear function of the density, or in other words the ethereal elasticity is in simple direct relation to the density;† rather simpler in the case of sulphuric than of nitric acid.

It is, of course, true that the range is very short, namely from  $\lambda = 434 \text{ } m\mu$  to  $\lambda = 656.3 \text{ } m\mu$ , approximately that of a major fifth in a musical scale, but restrictions are imposed by the limits of human vision and the particular

\* Fleming and Dewar, 'Roy. Soc. Proc.', vol. 61, p. 309, 1897, and vol. 62, p. 258, 1898.

† Cf. Larmor, 'Phil. Trans.', A, 1897, pp. 236 to 246.

method of experiment. The discrepancies for the ranges 0 to 3 per cent. and 95 to 100 per cent. are doubtless due to wholly different causes.

Similarly our observations show a sudden fall in the factors  $\Delta_{\mu\beta}/\Delta p$  and  $\Delta A/\Delta p$  at 97.3 per cent., proceeding to 98.7 per cent., followed by a rise at 99.3 per cent., namely, the curves for these factors and of density in terms of percentage are parallel.

Conversely for the factors  $\Delta R/\Delta p$ , commencing with a change at 95 per cent. there is an increase from this point up to 98 per cent., followed by a fall, or the curve for  $\Delta R/\Delta p$  in terms of  $p$  is the curve for  $d$  in terms of  $p$  inverted.

The constitution of sulphuric acid about 100 per cent.  $H_2SO_4$  has recently been discussed by Domke and Bein,\* and the conclusion arrived at is to the effect that there is no simple substance of the composition represented by the formula  $H_2SO_4$  (however convenient such an ideal substance may be for the purposes of computation), but that it is a mixture of molecules  $H_2SO_4$ ,  $SO_3$  and  $H_2O$  or  $H_3SO_5SO_3$ , or it may even contain pyrosulphuric acid  $H_2S_2O_7$ . In our former communication on the electric conductivity of nitric acid† from the irregularities observed we put forward the similar view that the substance represented by the formula  $HNO_3$  is also an ideal, and that it is a mixture of  $HNO_3$ ,  $N_2O_5$ , and  $H_2O$ .

It is to us a source of gratification to find ourselves so completely in accord with our fellow workers in another country, even in giving up familiar and possibly cherished notions.

#### *Summary.*

1. The refractive indices of sulphuric acid-water mixtures of concentration varying from rather under 1 per cent. to rather over 99 per cent. have been determined for the four lines  $H_\alpha$ ,  $D$ ,  $H$ ,  $H_\gamma$ , and the results compared in certain cases with the previous observations of van der Willigen.

2. The temperature coefficients, within practicable limits, have been measured, and these values used for reducing all the refractive indices to a common temperature of 15.

3. The maximum value of the refractive indices and of the first constant of Cauchy's formula occur at a point which corresponds approximately with the composition of the hydrate  $H_2SO_4H_2O$ , but otherwise any indication of the existence of other hydrates is doubtful.

4. Lorentz's factor,  $(\mu^2 - 1)/(\mu^2 + 2) d$ , is a linear function of the percentage up to 90 per cent., or in other words the ethereal elasticity is compensated by

\* *Loc. cit. supra.*

† 'Phil. Trans.', A, 1898, p. 365.

the density. There is, however, a slight alteration at about 30 per cent. concentration. The differences are given between the calculated and observed values for this factor as from an equation  $R' = R - a \Delta p$  in the case of the lines D and  $H_{\gamma}$ .

5. The refractive indices, the Cauchy constants and the Lorentz factor all show irregularities for concentrations 92 to 100 per cent., which are consistent among themselves, as also with a maximum density at about 97 per cent., and a minimum point between 99 and 100 per cent.

The question is, therefore, again raised as to whether a substance represented by a simple formula  $H_2SO_4$  does exist as a distinct entity, and a comparison is drawn herewith between nitric and sulphuric acids.

6. As an incidental point the effect of carbon dioxide and of silica upon the refractive index of water is discussed, but the final interpretation of the results left as a subject of further enquiry.

In conclusion we desire to express our obligations to the Kaiserliche Normal-Eichungs Kommission for sending their publications and the kindly interest which they have taken in our investigations, to Professors Elliott and Esson, to Dr. Messel, Mr. James Walker, and others who have rendered us assistance in matters of difficulty.

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